

FUNDAMENTALS OF CATALYSIS

M.K. Carter
Carter Technologies
P.O. Box 1852
Los Gatos, CA 95031

Keywords: theory of catalysis, transition probability, allowed catalysts

I. Background

Catalysis has been conducted for many years yet no fundamental understanding has emerged which teaches how to design a catalyst at a molecular level. Linus Pauling¹ stated, "It is thought that catalysts speed up reactions by bringing the molecules reacting together and holding them in configurations favorable to reaction." This definition offers a picture of what is to be achieved but does not suggest a mechanism of how catalysis might be accomplished. An alternative definition is proposed: *catalysis is a barrier free transformation from one electronic configuration to another.* This definition is presented as a starting point for a more formal development toward a goal of catalyst design at a molecular level. A true catalyst provides an orbital pathway for reactants to proceed to products such that the thermodynamic change in free energy for the reaction is negative. Thus, the act of catalysis will be treated as a radiationless stimulated emission - a natural transition from one electronic state to another.

II. Geometry

Consider the geometry of a set of atoms which compose a catalyst. Let r be the wave function of the reactant and let p be the wave function of the product. Catalytic conversion of a reactant to a product may be represented by a unitary transformation of r to p as $Ur = p$ so both the length of the vector and the symmetry of the wave function are preserved. This same unitary matrix transforms the wave function of the catalyst c such that $Uc = c$ since a catalyst returns to its original state following conversion of a reactant to a product. The column vectors of the unitary operator U were determined by expansion of the general form of a three by three unitary matrix to find the eigenvalues of $UU^\dagger = E$ so the value of the special function, c , could be calculated. The result is presented in figure 1 which shows the only geometric form allowed for a catalyst under such a unitary transformation is a one dimensional or linear geometric configuration. In this case its linear in the x -direction, but this axis is not unique. For example, catalysts represented by Y-M-Y for which M is a transition metal and Y is any appropriate electronegative atom, such as Cl-Mn-Cl or Co-Fe-Co, are described as being in linear geometric configurations. Should the molecule Y-M-Y be inherently non-linear, it may still exhibit catalytic activity during that fraction of time its bending vibration carries it through a linear configuration.

III. Symmetry Requirements

The symmetry of the reactant(s) associated with a catalyst is best described as belonging to a specific symmetry group. For example, carbon monoxide associated with a $M_1-M_2-M_1$ catalytic backbone, as required for Fischer-Tropsch catalytic conversion of CO/H_2 to hydrocarbons, may be represented as shown in figure 2. The two C-O molecules associated to the catalyst $M_1-M_2-M_1$ form a group described by the E , C_2 , i , S_2 , S_2' and σ_h classes of symmetry operations. These six operations form a special D_{2h} symmetry group as shown in the character table of figure 3. During the instant of catalysis an initial chemical transformation is caused by the shifting of electrons from the catalyst, figure 2A, to form metal-carbon and metal-oxygen sigma bonds, figure 2B. These geometrical configurations represent the individual functions of the degenerate basis E_{1g} . One of the two-fold degenerate wave functions represents bonding configuration A while the other describes bonding configuration B. The transformation from one degenerate level to the other may be described as a barrier free electron shift. From the form of the mutually degenerate representations $\Gamma(E_{1A})$ and $\Gamma(E_{1B})$ different cooperative electron bonding may be inferred. Thus, $\Psi_+ = (\Psi_{E_{1A}} + \Psi_{E_{1B}}) = 2\phi_1 - \phi_2 - \phi_3 - 2\phi_4 + \phi_5 + \phi_6$ results from the sum and $\Psi_- = (\Psi_{E_{1A}} - \Psi_{E_{1B}}) = -\phi_2 + \phi_3 + \phi_5 - \phi_6$ results from the difference of the doubly degenerate functions. The relative sign patterns are shown for both the sum and difference molecular functions in figures 2C and 2D. The sign of the wave function at carbon atoms 2 and 5 remains unchanged from Ψ_+ to Ψ_- . These atoms

represent expectations of the active catalytic sites. Since no change of sign is evident, then catalysis may proceed under the barrier free condition.

The symmetry of a propene-catalyst association also belongs to the special D_{2s} symmetry group. Propene associated with the catalytic site M_2 , refer to figure 4, may be represented where only one critical hydrogen atom is shown. Here the sign of the wave function on atoms 1 and 4 remains unchanged from Ψ_+ to Ψ_- . Thus, group symmetry considerations represent these two atoms as the expected catalytically activated sites. Experimental evidence shows the great majority of products formed during Ziegler-Natta catalysis do bond head-to-tail while the mechanism shows a tail-to-tail bond formation. This suggests a methylide and hydride exchange during an intermediate step to affect the apparent final head-to-tail bonded product.

IV. Transition Probability

A measure of the efficiency of catalysis may be determined by its transition probability, just as the intensity of a spectral line may be determined by its transition probability from one state to another allowed state. Such an electronic transition occurring between the product and reactant states Ψ_p and Ψ_r may be expressed by a quantum mechanical probability $|m_\mu|^2$ for which the transition moment m_μ is given by the expression

$$m_\mu = \int \Psi_p^* \mu \Psi_r d\tau$$

where μ is the amplitude of the induced electric moment. Einstein's transition probabilities⁵ are seen to be wholly applicable for describing the electronic transition of molecular catalysis. Computation of the transition moment can be conducted specifically by using the set of wave functions which represent a metal-carbon monoxide complex as expressed previously, namely

$$\begin{aligned} \Phi &= \Phi_a + \Phi_b + \Phi_c + \Phi_d \\ &= (1/N_2)[1/6\phi_{4s}^{Fe} + (2)^{1/2}/8\phi_{3dxz}^{Fe} + (2)^{1/2}/8\phi_{3dyz}^{Fe} + 1/8\phi_{3dxz}^{Fe} + \phi_{2py}^{O1} + \phi_{2pz}^{O1}]_a \\ &\quad + (1/N_2)[1/6\phi_{4s}^{Fe} - (2)^{1/2}/8\phi_{3dxz}^{Fe} - (2)^{1/2}/8\phi_{3dyz}^{Fe} - 1/8\phi_{3dxz}^{Fe} + \phi_{2py}^{O1} + \phi_{2pz}^{O1}]_b \\ &\quad + (1/N_2)[1/6\phi_{4s}^{Fe} - (2)^{1/2}/8\phi_{3dxz}^{Fe} - (2)^{1/2}/8\phi_{3dyz}^{Fe} + 1/8\phi_{3dxz}^{Fe} - \phi_{2py}^{O2} + \phi_{2pz}^{O2}]_c \\ &\quad + (1/N_2)[1/6\phi_{4s}^{Fe} + (2)^{1/2}/8\phi_{3dxz}^{Fe} - (2)^{1/2}/8\phi_{3dyz}^{Fe} - 1/8\phi_{3dxz}^{Fe} - \phi_{2py}^{O2} + \phi_{2pz}^{O2}]_d \end{aligned}$$

for which the normalization constant is $N_2 = (349)^{1/2}/6$. Here all of the valance orbital functions have been given specifically and each of the four quadrants of the molecular association for the complex have been enclosed in brackets for purposes of organization. The transition moment can be computed, one quadrant at a time, replacing μ by its operator r using the system wave functions Φ as

$$\begin{aligned} m_\mu^a &= \int \Phi_a^* r \Phi_a d\tau \\ &= \int_0^\infty \int_0^\pi \int_0^{2\pi} \Phi_a^* r \Phi_a r^2 \sin\theta \, d\phi \, d\theta \, dr \end{aligned}$$

Orthonormalized hydrogen-like one electron wave functions² were used and each of the four quadrant contributions to the transition moment was computed separately. The results by quadrant are

$$m_\mu = m_\mu^a + m_\mu^b + m_\mu^c + m_\mu^d = 0.2092110 + 0.2603221 + 0.2092110 + 0.2603221$$

$$\text{or } m_\mu = 0.9390517.$$

The value of the transition moment approaches unity supporting the requirement for a catalyst of linear geometric configuration constrained by a special D_{2s} symmetry group. Such strong transitions are not to be construed as oxidations or reductions since the time of a catalytically stimulated transition is expected to be less than the time of a molecular vibration ($< 10^{-14}$ second) following which the shifted electrons return to the original electronic configuration leaving new products in place of the reactants.

V. Catalyst Stabilization Against Permanent Oxidation

The external atoms M_1 - and $-M_3$ in the linear catalyst cluster $M_1-M_2-M_3$ are present to stabilize the oxidation state of the catalytic site $-M_2-$. These groups possess the same or greater electronegativity³ as $-M_2-$ and represent the only allowed condition for catalysts. This effect is described by positioning local dipoles along the bonds pointing toward the external atoms.

A set of allowed bimetal and centrally symmetric trimetal linear catalysts formed from first row transition metal series elements is presented in figure 5. Similar sets of linear strings of symmetry allowed catalysts can be formed from the second and third row transition metal series. Noncentrally symmetric catalysts, such as Fe-Mn-Cu and interseries catalysts, are also possible provided they conform to the requirements of the theory.

Different oxidation states are required for various types of catalysis. For example, Fischer-Tropsch conversions can be accommodated by strings of zero valent metals such as Fe-Fe and Fe-Fe-Fe while Ziegler-Natta reactions seem to require higher oxidation states such as the $Ti^{3+}-Ti^{3+}$ and $Ti^{3+}-Ti^{3+}-Ti^{3+}$ strings.

VI. Ab Initio Computation of the Energy of a Carbon Monoxide-Catalyst Complex

Strength of the bond between the associated reactant and the active site of the catalyst was considered for the case of a carbon monoxide pi-bonded to the iron atom. A three atom model was developed in which the associated carbon monoxide was positioned symmetrically with the iron atom. Bond distances of 1.830 Angstroms for the iron to carbon and iron to oxygen bonds, and 1.210 Angstroms for the carbon to oxygen bond were assigned. Molecular bond energies were computed using the Hartree-Fock formalism for an eighteen electron spin function for a closed-shell system⁴. The symmetry determined molecular wave function is the best representation for carbon monoxide pi-bonded to the iron atom. It was derived from the same symmetry determined valence electron function employed for the transition moment computation. A single cycle bonding energy of 2.5152 eV (58 kcal/mol) was computed for the complex. The energy level was doubly degenerate as anticipated by the symmetry requirement.

VII. Recent Applications

Generation of a theoretical model based on these ideas forms the basis for identification of specific molecular catalysts for selected chemical reactions through computational methods. Several catalysts have been prepared in the laboratory, based on this work, for use in Fischer-Tropsch conversions, ambient temperature oxidation of gasoline and diesel fuel in water, and other reactions. The Fischer-Tropsch catalyst Co-Fe-Co was responsible for formation of liquid hydrocarbons directly in the C_8 to C_{22} range. GC-MS and FTIR molecular spectra show the products to be linear aliphatic hydrocarbons, refer to figures 6. Approximately half a dozen Cu-Fe and Fe-Fe based oxidation catalysts of the form $Fe(CN)_2L_3-FeCl_2L_3$, for L being $K_2Cu(CN)_3$ and related ligands, were prepared for destruction of 20 ppm gasoline and 100 ppm diesel fuel in water in approximately 15 minutes. Refer to figure 7.

VIII. Conclusion

Recognition of a reasonable starting point in the form of a definition of catalysis, namely that *catalysis is a barrier free transformation from one electronic configuration to another*, has become a basis from which the fundamentals of catalysis have been developed. Application of these fundamentals has produced oxidation, Fischer-Tropsch and other catalysts which generated products at good rates at room temperature without prior thermal conditioning. It is hoped that this work will add to the existing body of catalysis knowledge and give industry new opportunities for development, and expanded growth in the future.

References

1. L. Pauling, General Chemistry, W.H. Freeman & Company, San Francisco, 1959, 2nd ed., p115.
2. L. Pauling and E.B. Wilson, Introduction to Quantum Mechanics, McGraw-Hill Book Co., New York, 1935, p 302.
3. L. Pauling, J.Am.Chem.Soc. 1932, 54, 3570.
4. W.J. Hehre, L Radom, P.v.R. Schleyer and J.A. Pople, Ab Initio Molecular Orbital Theory, pub. John Wiley & Sons, New York, 1986, p21.

$$Uc = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{vmatrix} \begin{vmatrix} 1 \\ 0 \\ 0 \end{vmatrix}$$

Figure 1. Geometric Vector For A Catalyst

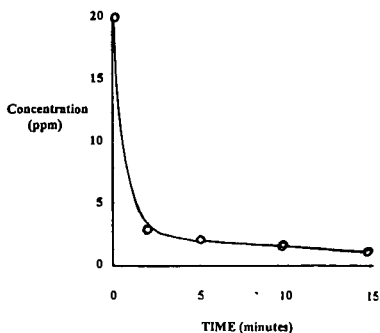


Figure 7. Oxidative Destruction Of Gasoline

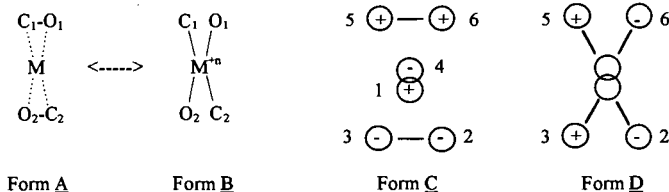


Figure 2. Degenerate Bonding Functions And Signs For Carbon Monoxide On A Catalyst

| D_{2s} | E | C_2 | i | S_2' | S_2'' | σ_h | | |
|---|-----|-------|-----|--------|---------|------------|---------------------|--|
| A | 1 | 1 | 1 | 1 | 1 | 1 | z, R_z | $\alpha_{xz} + \alpha_{yz}, \alpha_{xz}$ |
| B | 1 | 1 | 1 | -1 | -1 | -1 | | |
| E_1 | 2 | -1 | -1 | -2 | 1 | 1 | $(x, y) (R_x, R_y)$ | α_{xz}, α_{yz} |
| E_2 | 2 | -1 | -1 | 2 | -1 | -1 | | $\alpha_{xz} - \alpha_{yz}, \alpha_{xy}$ |
| $\Gamma(\text{sum})$ | 6 | 0 | 0 | 0 | 0 | 0 | | |
| $\Gamma(\alpha) = \Gamma(A) \times \Gamma(E_1)$ | 2 | -1 | -1 | -2 | 1 | 1 | $= \Gamma(E_1)$ | |

The direct product of irreducible representations describing the polarizability matrix, α , is $\Gamma(A) \times \Gamma(E_1) = \Gamma(E_1)$ which is also irreducible.

Figure 3. Character Table For Special D_{2s} Symmetry Group

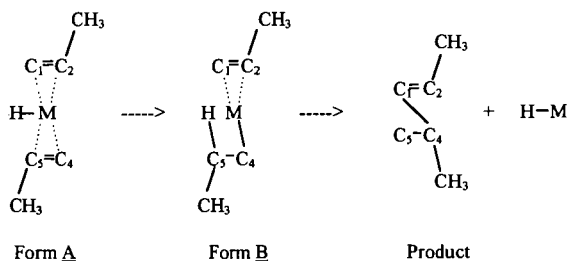


Figure 4. Barrier Free Symmetry Selected Bonding For Ethylene Dimerization

| | | | | | | | |
|-------|-------|-------|----------|----------|----------|----------|----------|
| Ti-Ti | Mn-Ti | Co-Cr | Ni-Ti | Ni-Cu-Ni | Ni-Fe-Ni | V-Cr-V | Ni-V-Ni |
| V-V | Fe-Fe | Co-V | Cu-Cu | Cu-Cu-Cu | Cu-Fe-Cu | Cr-Cr-Cr | Cu-V-Cu |
| V-Ti | Fe-Mn | Co-Ti | Cu-Ni | Co-Ni-Co | Ti-Mn-Ti | Fe-Cr-Fe | Ti-Ti-Ti |
| Cr-Cr | Fe-Cr | Ni-Ni | Cu-Co | Ni-Ni-Ni | V-Mn-V | Co-Cr-Co | V-Ti-V |
| Cr-V | Fe-V | Ni-Co | Cu-Fe | Cu-Ni-Cu | Cr-Mn-Cr | Ni-Cr-Ni | Cr-Ti-Cr |
| Cr-Ti | Fe-Ti | Ni-Fe | Cu-Mn | Co-Co-Co | Mn-Mn-Mn | Cu-Cr-Cu | Mn-Ti-Mn |
| Mn-Mn | Co-Co | Ni-Mn | Cu-Cr | Ni-Co-Ni | Fe-Mn-Fe | V-V-V | Fe-Ti-Fe |
| Mn-Cr | Co-Fe | Ni-Cr | Cu-V | Cu-Co-Cu | Co-Mn-Co | Cr-V-Cr | Co-Ti-Co |
| Mn-V | Co-Mn | Ni-V | Cu-Ti | Fe-Fe-Fe | Ni-Mn-Ni | Fe-V-Fe | Ni-Ti-Ni |
| | | | Co-Cu-Co | Co-Fe-Co | Cu-Mn-Cu | Co-V-Co | Cu-Ti-Cu |

Figure 5. Allowed Bi and Symmetric Trimetal First Row Transition Metal Linear Catalysts

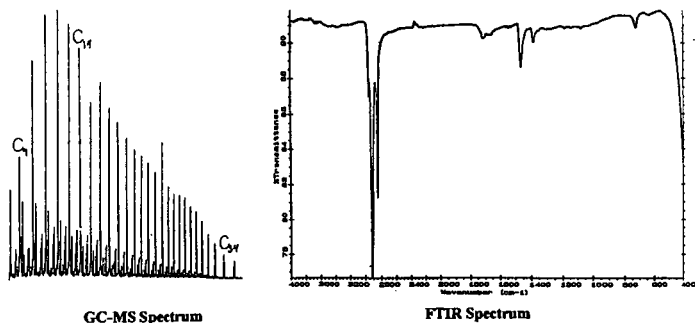


Figure 6. GC-MS And FTIR Molecular Spectra Of Fischer-Tropsch Aliphatic Hydrocarbons